

(19) World Intellectual Property Organization International Bureau

(43) International Publication Date
17 November 2005 (17.11.2005)

PCT

(10) International Publication Number
WO 2005/108673 A1(51) International Patent Classification⁷: D21C 9/16, 9/10, 5/02

(21) International Application Number: PCT/FI2005/000211

(22) International Filing Date: 10 May 2005 (10.05.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 20040673 12 May 2004 (12.05.2004) FI

(71) Applicant (for all designated States except US): KEMIRA OYJ [FI/FI]; Porkkalankatu 3, FI-00180 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): PARÉN, Aarto [FI/FI]; Verkkokatu 3 A 5, FI-65230 Vaasa (FI). AHLGREN, Jonni [FI/FI]; Karitie 11 F 45, FI-65230 Vaasa (FI). JÄKÄRÄ, Jukka [FI/FI]; Männistökuja 1 B 52, FI-33410 Tampere (FI). RENVALL, Ilkka [FI/FI]; Puronvarsi 4 B, FI-02300 Espoo (FI). RAUTIAINEN, Jukka [FI/FI]; Säterinkatu 9 A 19, FI-02600 Espoo (FI).

(74) Agent: BERGGREN OY AB; P.O. Box 16, (Jaakonkatu 3 A), FI-00101 Helsinki (FI).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

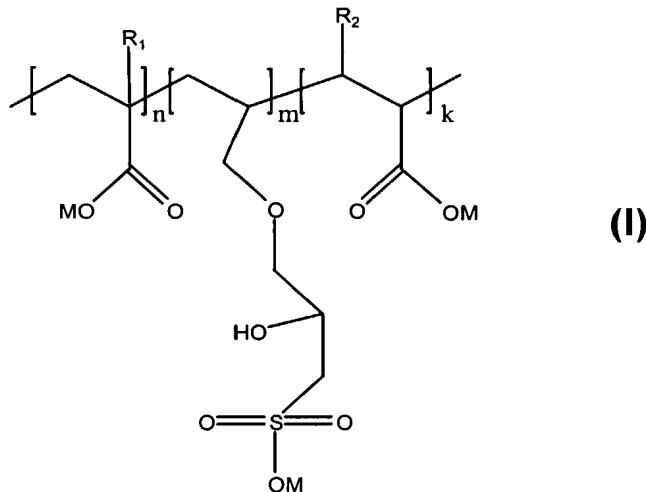
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: NEW COMPOSITION AND PROCESS FOR THE TREATMENT OF FIBRE MATERIAL



(57) Abstract: The present invention relates to a stabilizing composition comprising following components (A) a polymer having following formula (I) wherein R₁ is a hydrogen atom or an alkyl group containing 1 to 12 carbon atoms, R₂ is -COOM or -CH₂COOM, M is a hydrogen atom, an alkali metal ion, an alkaline earth metal ion, an ammonium ion or a mixture thereof, n, m and k are molar ratios of corresponding monomers, wherein n is 0 to 0.95, m is 0.05 to 0.9, and k is 0 to 0.8, and (n+m+k) equals 1, and the weight average molecular weight is between 500 and 20,000,000 g/mol, (B) a chelating agent, and (C) an alkaline earth metal compound. The invention also relates to a process for the treatment of a fibre material.

New composition and process for the treatment of fibre material

Field of the invention

The present invention relates to a composition comprising a polymer, a chelating agent and an alkaline earth metal compound and to a process for the treatment of a fibre material, especially a cellulosic fibre material in the presence of a polymer, a chelating agent and an alkaline earth metal compound. The composition can be used as a pretreatment in the bleaching with a peroxygen compound of chemical, mechanical, chemi-mechanical and de-inked pulps and as a pretreatment in deinking of recycled fibers and in alkaline peroxide bleaching of mechanical, chemical, chemi-mechanical and de-inked pulps. The composition can also be used in deinking of recycled fibers. The composition replaces partly or totally silicate as a stabilizer, especially in the treatment of mechanical and deinked pulps. The present invention also relates to a process for bleaching a cellulosic fibre material with a peroxide compound in an aqueous alkaline medium by using said composition.

Description of the Related Art

It is well-known that chelating agents can be used as pretreatment for removing harmful metal ions, i.e. generally such transition metal ions as iron and manganese before pulp is bleached with a peroxygen compound, such as hydrogen peroxide, peracetic acid or Caro's acid. In alkaline peroxide bleaching of mechanical pulps, in bleaching of de-inked pulp (DIP) made from recovered waste paper and in the deinking of recovered waste paper, water glass (alkali silicate) and a chelating agent can be added.

Since the common chelating agents such as polyaminopolycarboxylates, e.g. EDTA and DTPA and the corresponding methylenephosphonic acid derivatives of the polyamines are non-biodegradable or show a low biodegradation, there is a target to decrease the use of the common chelating agents as pretreatment agents.

Alkaline silicate solutions normally called water glass have been used in stabilizing hydrogen peroxide solutions, which are used in alkaline peroxide bleaching of mechanical pulps.

Water glass is used alone or together with peroxide in de-inking of recovered papers. Sometimes the de-inked pulp is also bleached with alkaline peroxide.

The use of water glass in alkaline peroxide bleaching of chemical pulps has been published, but the method cannot be utilized in full scale, since the silicate can 5 cause very severe precipitation problems. Another disadvantage with water glass is that when the bleaching liquors are recycled and ultimately fed into the recovery boiler, where the so-called black liquor from the cooking process after concentration is burned, the silicate will cause severe scaling and thus decrease the heat transfer in the recovery boiler, which in worst case can cause an 10 explosion of the recovery boiler.

If the silicates, e.g. in form of the water carry-over, will enter the paper making process, they will disturb the papermaking process, e.g. by precipitating on hot surface, causing holes in the paper reel etc.

It is known that hydrogen peroxide will decompose very rapidly in an alkaline 15 milieu in the presence of transition metal ions. The most abundant of these ions in pulps are iron and manganese. The copper ion is also very detrimental for alkaline hydrogen peroxide, but normally it can enter the process only via used process waters.

It is also known that iron will start to precipitate already below pH 7, first in colloidal 20 form. The formed iron hydroxides, oxyhydroxides etc are much more catalytically active than iron ions. Also manganese can, at least partly, be in precipitated form, but it has been shown that in the presence of hydrogen peroxide, manganese should be in dissolved form.

The theory of the function of water glass varies, but one theory is that water glass 25 will deactivate the catalytic surface of iron and other heavy metal ion "precipitates". In order to avoid the detrimental effect of manganese ions, a chelating agent is often introduced into the bleaching process or the pulp is pretreated with a chelating agent. The most common chelating agents are EDTA and DTPA, which belong to the group of polyaminopolycarboxylates. The corresponding phosphonates, EDTMPA and DTPMPA can also be used, but they are much more expensive 30 than the polyaminopolycarboxylates. They have also the disadvantage that they contain phosphorus, which is not a wanted component, when the environmental regulations are becoming stricter and stricter.

In the deinking of waste paper, water glass has also other functions, e.g. water glass improves ink detachment, it will disperse the ink and act as a buffer keeping the pH constant. Therefore a partly replacement of water glass would also be advantageous and at the same time decrease the precipitation problems
5 connected with the use of water glass.

According to the above there is a need to partly or totally replace water glass (silicates) in alkaline peroxide bleaching processes and in pulping processes, which use water glass, e.g. in alkaline peroxide bleaching of mechanical and de-linked pulps and in de-inking of recovered paper. There have been suggestions to
10 use phosphonates, but they should be used in quite high dosages and the phosphorus problem in the waste waters would still remain. Since the common phosphonates are non-biodegradable, there has been much studies about they
15 adverse effect on mobilizing heavy metals, e.g. from sediments in waterways. If phosphonates would be used, the dosage of these substances should be decreased.

A pretreatment method for bleaching pulp with hydrogen peroxide in alkaline conditions in the presence of sodium silicate and adding 0.05-1% by weight (based on dry pulp) of a copolymer of 3-allyloxy-2-hydroxypropanesulfonic acid (AHPS) and (meth)acrylic acid in the pretreatment is described in the Japanese
20 patent publication JP 1266295 (published 24 October 1989).

According to the Japanese patent application JP 1148890 (published 12 June 1989) the same kind of polymer in an amount of 0.05-1% by weight (based on dry pulp) has been used instead of e.g. DTPA in alkaline peroxide bleaching. In JP 1148890 the bleaching performance of a number of different AHPS-acrylic acid
25 copolymers are shown and compared e.g. with the performance of DTPA.

In the both JP patent applications the tested amounts are very big, since normally the chelating agents are used in an amount of 0.5 to 2 kg per ton pulp as 100% sodium salt.

Finnish unpublished patent application FI-20040293 discloses a process for
30 bleaching a fibre material with an alkaline peroxide solution in the presence of a chelating agent and a copolymer of 3-allyloxy-2-hydroxypropanesulfonic acid (AHPS) with (meth)acrylic acid, maleic acid or itaconic acid. This patent application also discloses a composition comprising said copolymer and the

chelating agent for use as a stabilizer in alkaline peroxide bleaching for replacing partly or totally water glass.

Summary of the present invention

According to the present invention it has now surprisingly been found that by using 5 a copolymer of AHPS and an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, maleic acid or itaconic acid, together with a chelating agent and an alkaline earth metal compound, such as magnesium sulphate, either mixed together or added separately, a very good bleaching performance can be achieved and a total replacement of water glass can be achieved, if necessary from the 10 pulping and paper making point of view. Surprisingly, the combination of the copolymer, the chelating agent and the alkaline earth metal compound showed an improved effect as compared to the effect of the combination of the copolymer and the chelating agent or the combination of the chelating agent and the alkaline earth metal compound. Test results unexpectedly showed a clear synergistic 15 effect.

The combination of the three components, i.e. the copolymer, the chelating agent and the alkaline earth metal compound, can very effectively be used as a stabilizer in bleaching of a chemical, mechanical or de-inked pulp with a peroxygen compound, such as hydrogen peroxide, peracetic acid or Caro's acid. The present 20 invention makes it possible to partially or totally replace water glass in bleaching and deinking processes by using the combination of the three components.

The present invention provides a process for treatment of a fibre material comprising the step of contacting the fibre material in an aqueous medium with a chelating agent, the above copolymer and an alkaline earth metal compound. The 25 copolymer, the chelating agent and the alkaline earth metal compound can be added separately or preferably as a ready made mixture (composition).

The present invention also relates to a composition comprising the copolymer, the chelating agent and the alkaline earth metal compound.

The composition and process according to the invention can be used as a 30 pretreatment of all kind of pulps, chemical pulps, mechanical, chemi-mechanical pulps and deinked pulps, which are bleached with alkaline peroxide.

The composition and process according to the invention can also be used in the bleaching of all kind of pulps, chemical pulps, mechanical, chemi-mechanical pulps and deinked pulps by using hydrogen peroxide as the bleaching agent.

5 The composition and process are also suitable in deinking of recycled pulps, in which water glass and hydrogen peroxide are commonly used.

The composition can also be used in sodium dithionite bleaching of mechanical and de-inked pulps.

10 The alkaline peroxide bleaching process for mechanical, chemi-mechanical and de-inked pulps according to the invention can be practiced as a single stage of bleaching or in a two-stage process, where the pre-bleached pulp is entering the second stage. Any consistency can be used, but it is most preferable to use medium consistency in the first stage and high consistency in the second stage.

15 If needed, the bleaching can be preceded by a pretreatment with a chelating agent or preceded by a pretreatment according to the invention in order to reduce the amount of transition metals entering the bleaching process.

20 In the de-inking process the composition of the present invention can be used in repulping or in a disperger or in a kneader which possibly is followed by a soaking tower whereto hydrogen peroxide can be fed. In the de-inking process the composition of the present invention can also be used in a separate bleaching stage or any process stage where hydrogen peroxide is present.

The composition, either as ready made mixture or as combination of the three components, can be used as total or partial replacement in those processes, where water glass are commonly used.

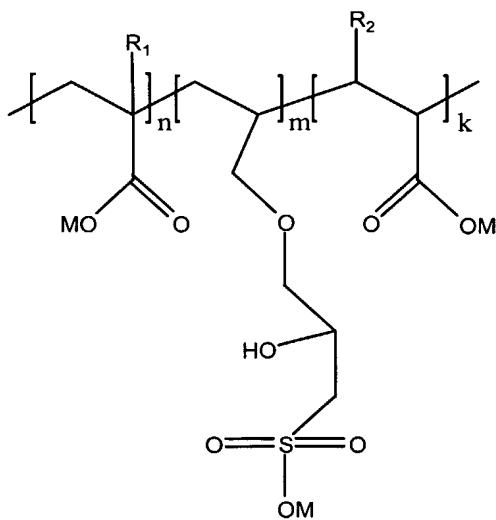
25 The theory how the three components will work together is not clear, since the polymer itself cannot stabilize very well alkaline hydrogen peroxide solutions and also gives in general poor bleaching performance. Nor does the alkaline earth metal compound stabilize alkaline hydrogen peroxide solutions very well especially in the presence of manganese. The chelating agents stabilize quite well the above mentioned alkaline peroxide, but cannot give a good bleaching result. The 30 common chelating agents mentioned above, will bind the soluble manganese ions in the alkaline peroxide solutions, but since iron is then in solid form, either colloidal or in precipitated form, chelating agents cannot any more bind the solid compounds. The same is valid for the solid forms of manganese compounds. The

polymer somehow binds to the solid surfaces or inactivates the catalytic effect of the solid particles. Thus a combined effect will be obtained. The common chelating agents cannot, when used alone, give a good bleaching performance, i.e. for chemical pulps, small viscosity loss and high brightness gain and a sufficient amount of residual peroxide, and for mechanical pulps and deinked pulps high brightness gain and a sufficient amount of residual peroxide, which indicates that peroxide has mainly been consumed for bleaching and not for decomposition processes. Therefore there must be some synergistic effect between the three components used according to the invention.

10 Detailed description of the invention

In a first aspect of the present invention there is provided a stabilizing composition comprising following components

(A) a polymer having following formula



15 wherein

R_1 is a hydrogen atom or an alkyl group containing 1 to 12 carbon atoms,

R_2 is $-COOM$ or $-CH_2COOM$,

M is a hydrogen atom, an alkali metal ion, an alkaline earth metal ion, an ammonium ion or a mixture thereof,

20 n , m and k are molar ratios of corresponding monomers, wherein n is 0 to 0.95, m is 0.05 to 0.9, and k is 0 to 0.8, and $(n+m+k)$ equals 1, and

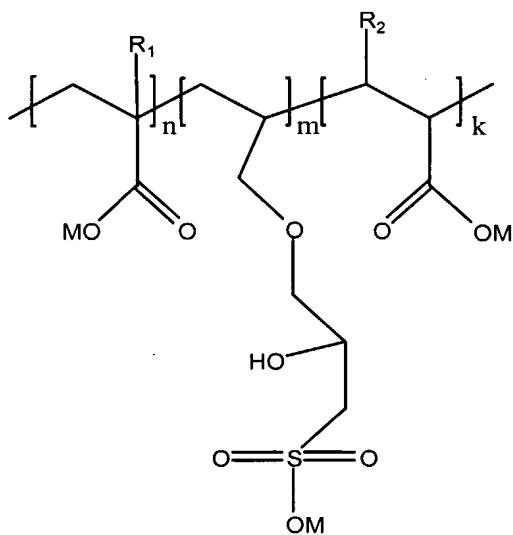
the weight average molecular weight is between 500 and 20,000,000 g/mol,

(B) a chelating agent, and

(C) an alkaline earth metal compound.

In a second aspect of the present invention there is provided a process for the
5 treatment of a fibre material comprising the step of contacting the fibre material in
an aqueous medium with following components

(A) a polymer having following general formula



wherein

10 R₁ is a hydrogen atom or an alkyl group containing 1 to 12 carbon atoms,

R₂ is -COOM or -CH₂COOM,

M is a hydrogen atom, an alkali metal ion, an alkaline earth metal ion, an ammonium ion or a mixture thereof,

15 n, m and k are molar ratios of corresponding monomers, wherein n is 0 to 0.95, m is 0.05 to 0.9, and k is 0 to 0.8, and (n+m+k) equals 1, and

the weight average molecular weight is between 500 and 20,000,000 g/mol,

(B) a chelating agent, and

(C) an alkaline earth metal compound.

The composition of the present invention can be used as a stabilizer in the bleaching of a fibre material in an aqueous medium or as a stabilizer in the deinking of a recycled fibre material.

5 The above alkali metal ion is preferably sodium or potassium ion, and the alkaline earth metal ion is preferably magnesium ion.

A preferred comonomer with AHPS is acrylic acid ($R_1=H$), methacrylic acid ($R_1=CH_3$), maleic acid ($R_2=COOM$) or itaconic acid ($R_2=CH_2COOM$). When k is 0 in formula I the preferred comonomer is acrylic acid or methacrylic acid, and when 10 n is 0 the preferred comonomer is maleic acid or itaconic acid. When both k and n are not 0 the preferred comonomers with AHPS are (meth)acrylic acid and maleic acid or itaconic acid.

The monomers are randomly distributed along the polymer chain of formula I, and preferably n is 0.4 to 0.9, m is 0.1 to 0.5, and k is 0 to 0.5.

If the system in pretreatment or in alkaline peroxide bleaching contains high 15 amount of calcium ions, as is the case, when so-called white water from papermaking process is circulated to the pulping and/or bleaching operations, it is advantageous to use maleic acid or itaconic acid ($k > 0$) as one of the comonomers in order to increase the calcium binding ability of the polymer. It is preferable in normal cases that the polymer only contains AHPS and a monomer 20 containing one carboxylic acid, such as acrylic acid, since a copolymer comprising multiple monomers is usually more difficult to produce.

The weight average molecular weight of the copolymer of formula I should be between 500 and 20,000,000 g/mol, preferably between 1,000 and 1,000,000 g/mol and most preferably between 2,000 g/mol and 500,000 g/mol.

25 If the weight average molecular weight is lower than about 500 g/mol, the efficiency of the polymer becomes too low. If the average molecular weight is higher than 20,000,000 g/mol, handling and dosage become a problem due to high viscosity of the polymer solution.

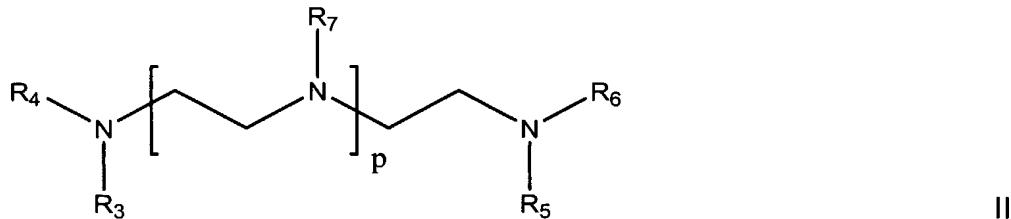
30 To increase the molecular weight of the copolymer and/or to enhance the efficiency of the copolymer, a cross linker may be used in an amount of 0 to 20 % by mole, preferably 0 to 10 % by mole, of the total monomer content. Suitable cross linkers are, for example methylenebisacrylamide, ethylene glycol divinyl

ether, di(ethylene glycol) divinyl ether, tri(ethylene glycol) divinyl ether and vinyl or allyl terminated polymers, but are not limited to these.

To decrease molecular weight of the copolymer and/or to enhance the efficiency of the copolymer, a chain transfer agent may be used in an amount of 0 to 20 % by 5 mole, preferably 0 to 10 % by mole, of the total monomer content. Suitable chain transfer agents are, for example thiols (e.g. butylmercaptan) and alcohols (e.g. isopropanol), but are not limited to these.

The chelating agent (B) to be used together with the copolymer (A) of formula I may be a chelating having formula II, III or IV below.

10 A preferred chelating agent is a compound having following general formula



wherein

p is 0 or an integer of 1 to 10,

15 R₃, R₄, R₅, R₆ and R₇ are independently a hydrogen atom or an alkyl chain having 1 to 6 carbon atoms and containing one or more active chelating ligands, such as carboxylic, phosphonic or hydroxyl group(s) or a salt thereof.

The alkyl chain is preferably methylene –CH₂– or ethylene –CH₂CH₂–.

In formula II R₃, R₄, R₆ and R₇ preferably represent the same group.

20 Examples of chelating agents according to the above formula II are polyaminopolycarboxylic acids and polyaminopolymethylenephosphonic acids.

The polyaminopolycarboxylic acids can be produced by the conventional route from the polyamine and formaldehyde and sodium cyanide or hydrocyanic acid. The more suitable route for small scale production is to use a haloacetic acid, especially monochloroacetic acid as a reactant.

Preferred polyaminopolycarboxylic acids are:

DTPA: $p=1, R_3 = R_4 = R_5 = R_6 = R_7 = -CH_2COOH$

TTHA: $p=2, R_3 = R_4 = R_5 = R_6 = R_7 = -CH_2COOH$

EDTA: $p=0, R_3 = R_4 = R_5 = R_6 = -CH_2COOH$

5 HEDTA: $p=0, R_3 = R_4 = R_5 = -CH_2COOH, R_5 = -CH_2CH_2OH$

EDDS: $p=0, R_3 = R_5 = H, R_4 = R_6 = -CH(COOH)CH_2COOH$
(ethylenediaminedisuccinic acid)

The polyaminopolymethylenephosphonic acids are made conventionally from the corresponding polyamine, formaldehyde and phosphonic acid. With the higher

10 amines a full substitution with acetic acid groups or methylenephosphonic acid groups will become more and more difficult. These chelating agents will also perform well in the composition but an incomplete substitution will make the chelating agents more prone for decomposition by hydrogen peroxide.

Preferred polyaminopolymethylenephosphonic acids are:

15 DTPMPA: $p=1, R_3 = R_4 = R_5 = R_6 = R_7 = -CH_2POO_2H_2$

TTHMPA: $p=2, R_3 = R_4 = R_5 = R_6 = R_7 = -CH_2POO_2H_2$

EDTMPA: $p=0, R_3 = R_4 = R_5 = R_6 = -CH_2POO_2H_2$

Another preferred chelating agent is a compound having following general formula



20 wherein

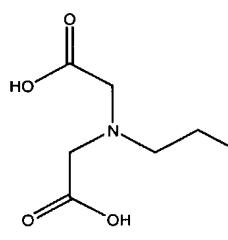
q is an integer of 3 to 10,

R_3, R_4, R_5 and R_6 are independently a hydrogen atom or an alkyl chain having 1 to 6 carbon atoms and containing one or more active chelating ligands, such as carboxylic, phosphonic or hydroxyl group(s) or a salt thereof.

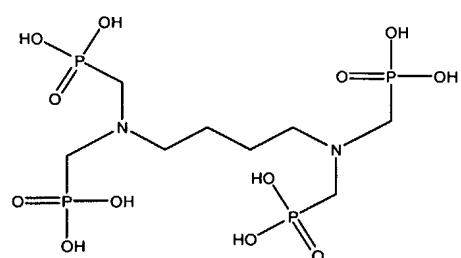
The alkyl chain is preferably methylene $-\text{CH}_2-$ or ethylene $-\text{CH}_2\text{CH}_2-$.

In formula III R_3 , R_4 and R_6 preferably represent the same group.

Examples of chelating agents according to the above formula III are the commercially available hexamethylenediamine tetra(acetic acid) ($q=6$) and 5 tetramethylenediamine tetra(methylenephosphonic acid) ($q=4$) having following formulae.



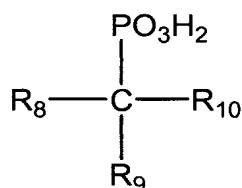
hexamethylenediamine tetra(acetic acid)



tetramethylenediamine tetra(methylenephosphonic acid)

Yet another preferred chelating agent is a compound having following general formula

10



IV

wherein

R_8 is a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms or an alkyl chain having 1 to 6 carbon atoms and containing a carboxylic, phosphonic or

15 hydroxyl group,

R_9 is a hydrogen atom, hydroxyl group, phosphonic group, carboxylic group or alkyl chain having 1 to 6 carbon atoms and containing one or two carboxylic groups, and

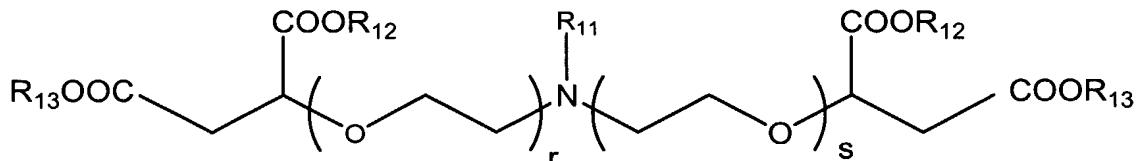
R_{10} is a hydrogen atom, hydroxyl group, carboxylic group, alkyl group containing 1

20 to 6 carbon atoms or alkyl chain having 1 to 6 carbon atoms and containing a carboxylic group, or a salt thereof.

The alkyl chain is preferably methylene $-\text{CH}_2-$ or ethylene $-\text{CH}_2\text{CH}_2-$.

An example of the non-nitrogen containing chelating agents according to the above formula IV is 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP).

5 A further preferred chelating agent is a compound having following general formula



V

wherein R_{11} is

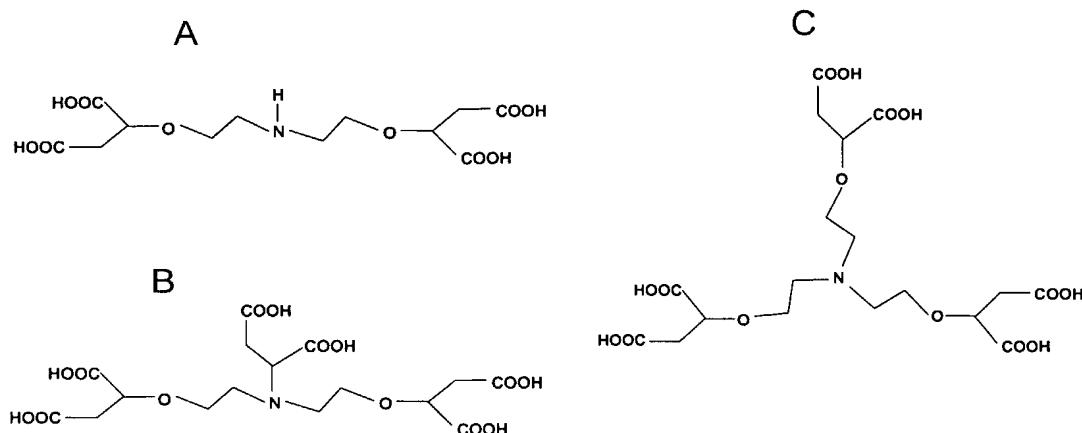
a hydrogen atom

10 an alkyl chain containing 1-30 carbon atoms,
 an alkyl chain containing 1-30 carbon atoms and 1-10 carboxylic acid groups attached to said chain, or alkali or alkaline earth metal salt thereof,
 an alkyl chain containing 1-30 carbon atoms and 1-10 carboxylic acid esters attached to said chain,

15 a (poly)ethoxylated hydrocarbon chain containing 1-20 ethoxyl groups, or
 a carboxylic acid amide containing 1-30 carbon atoms, where $\text{N}-\text{R}_{11}$ bond is an amide bond,
 R_{12} and R_{13} are: hydrogen, an alkali metal ion or an alkaline earth metal ion or an alkyl group containing 1-30 carbon atoms,

20 r is 0 or 1, and
 s is 0 or 1.

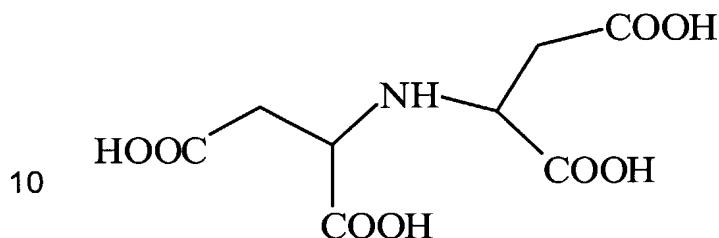
Preferred N-bis- or tris-[(1,2-dicarboxy-ethoxy)ethyl]amines of formula V are following



A = N-bis[(1,2-dikarboxy-ethoxy)-ethyl]-amine
B = N-bis[(1,2-dikarboxy-ethoxy)-ethyl]-aspartic (AES)
C = N-tris[(1,2-dikarboxy-ethoxy)-ethyl]-amine

5

A preferred N-bis-(1,2-dicarboxy-ethyl)amine of formula V is iminodisuccinic acid (ISA) having following formula



ISA

Though the formulas of the chelating agents are depicted above as acids, they are 15 commercially normally sold as their alkali salts, mainly as their sodium salts and the formulas given above have to be understood as including both the free acids and their salts.

The alkaline earth metal compound (C) to be used together with the copolymer (A) of formula I and the chelating agent (B) is preferably a magnesium or a calcium 20 compound or a mixture thereof, more preferably a magnesium compound. Especially preferred are water-soluble magnesium or calcium salts, such as magnesium or calcium chloride, sulphate or acetate or a mixture thereof, most preferably magnesium sulphate. According to the present invention the alkaline

earth metal can also exist as a complex with the chelating agent, especially an Mg-chelating agent complex, such as Mg-DTPA complex. The form of the alkaline earth metal in the stabilizer mixture has no effect here.

5 The polymer and the chelating agent can be added separately or as a composition mixture. The weight ratio of the polymer (calculated as solids) to the chelating agent (calculated as 100% chelating agent as sodium salt) is preferably from 1:4 to 4:1, more preferably from 1:3 to 3:1.

The alkaline earth metal compound can be added separately or as a composition mixture with the polymer or the chelating agent or both.

10 The total amount of the polymer (as solids), the chelating agent (as 100% sodium salt) and the alkaline earth metal compound (as alkaline earth metal) added separately or as a mixture, is preferably 0.05 - 10 kg per ton of dry fibre material, more preferably 0.1 - 5 kg per ton of dry fibre material, and most preferably 0.2 to 4 kg per ton of dry fibre material.

15 The amount of the polymer is preferably 0.05 - 5 kg per ton dry fibre material, more preferably 0.1 – 2 kg per ton dry fibre material calculated as solids.

The amount of the chelating agent is preferably 0.05 - 5 kg per ton dry fibre material, more preferably 0.1 - 2 kg per ton dry fibre material calculated as 100% sodium salt.

20 The amount of the alkaline earth metal compound is preferably 0.05 - 5 kg per ton dry fibre material, more preferably 0.1 – 2 kg per ton dry fibre material calculated as alkaline earth metal.

25 Preferably the three components (A), (B) and (C) are present in following weight ratios 10 to 60 : 20 to 70 : 10 to 50, more preferably 15 to 55 : 25 to 65 : 15 : 45, most preferably 20 to 50 : 30 to 60 : 20 to 40 calculated as active substance.

The fibre material is preferably a cellulosic fibre material, especially a chemical, mechanical, chemi-mechanical or deinked pulp. The cellulosic fibre material can also be any regenerated cellulose material, such as viscose, or flax or cotton.

30 If a composition mixture is made according to the invention, the normal content of active materials in the mixture can be at least 10%, preferably at least 15%, and

more preferably at least 20% by weight, but also more diluted solutions can be used in the application process.

In one embodiment of the process of the present invention the treatment comprises bleaching the fibre material with an alkaline peroxide solution in the 5 presence of the chelating agent, the polymer and the alkaline earth metal compound.

The bleaching of chemical pulp can be carried out at temperatures of from 50°C to 150°C and at all practical consistencies. The residence time in the bleaching can 10 vary within a wide range, from 30 to 240 minutes, preferably from 45 to 180 minutes and most preferably from 60 to 120 minutes. The residence time will also depend on the temperature used in the bleaching.

The stages can also be reinforced with oxygen, the abbreviation of stages depicted in the professional literature as EOP, Eop, PO or OP.

The peroxide bleaching of mechanical pulps with the process according to the 15 invention can comprise all kind of mechanical pulps, e.g. stone groundwood pulp (SGW), refiner mechanical pulp (RMP), pressure groundwood (PGW), thermo-mechanical pulp (TMP), but also chemically treated high-yield pulps such as chemithermomechanical pulp (CTMP). The invention is also useful in bleaching of deinked pulps. Deinked pulp can be made using mixed office waste (MOW), 20 newsprint (ONP), magazines (OMG) etc. as raw material and the composition of the present invention can be used in any process stage where peroxide is used. The invention can also be practiced in refiner bleaching of mechanical pulps and in alkaline peroxide mechanical pulp (APMP), in which wood chips are impregnated 25 with alkaline peroxide solution before refining. In these applications the invention is very advantageous, since the biggest obstacle to use hydrogen peroxide in these applications has been that water glass cannot be used, since the sodium silicate will e.g. fasten to the refiner plates and thus making the process unpractical.

The residence time in the bleaching can vary within a wide range, from 30 to 240 minutes, preferably from 45 to 180 minutes and most preferably from 60 to 120 30 minutes. The residence time will also depend on the temperature used in the bleaching.

The composition according to the invention can be used as a mixture or the ingredients can be added separately.

The bleaching of mechanical pulps can be carried out at a temperature of from 30°C to 90°C, preferably at a temperature of from 50°C to 90°C. The bleaching can be carried out at a consistency of choice, but it is most preferably to carry out the bleaching at a high consistency, i.e. about 30% or higher. Bleaching can also

5 be carried in two stages with a dewatering stage between the stages. The stages can be carried out at a consistency of choice, but it is most preferably to use medium consistency in the first stage and a high consistency in the second stage. This makes it possible to remove the detrimental substances efficiently.

The bleaching stage can be preceded by a chelating agent stage or a

10 pretreatment according to the invention, discussed in more detail below, and dewatering and thus improve the bleaching performance. In the chelating agent stage any of the above defined chelating agents can be used.

The ratio between the alkali and hydrogen peroxide can vary in a wide range, depending on raw materials and degree of bleaching. Also alternative alkali

15 sources, like sodium carbonate, can be utilized. The use of sodium carbonate is especially preferably to use, at least as a partial replacement of sodium hydroxide, when wastepaper is deinked with the total replacement of water glass using the composition according to the invention. The necessary buffer capacity can be ensured in this way.

20 In another embodiment of the process of the present invention the treatment comprises pretreating the fibre material in the aqueous medium comprising the chelating agent, the polymer and the alkaline earth metal compound.

The pretreatment according to the invention can be utilized for all kind of chemical and mechanical pulps.

25 The pretreatment can be followed by a bleaching with a peroxygen compound optionally in the presence of the chelating agent, the polymer and the alkaline earth metal compound. The peroxygen compound can be hydrogen peroxide, peracetic acid or Caro's acid.

30 The pretreatment of chemical pulps can also precede such stages, in which another peroxygen chemical than hydrogen peroxide is used, e.g. a peracetic acid, Caro's acid etc. stage. If the stage is followed by an alkaline stage comprising the use of hydrogen peroxide, the treatment can also be carried out after the above mentioned peroxygen stage. Depending on the raw material and the process the treatment can also be carried out only after the mentioned peroxygen stage.

The consistency of this pretreatment is preferably around 10% in order to ensure an efficient metal removal. The pH is preferably from 3 to 7, more preferably from 4 to 6.5 and most preferably from 4.5 to 6. The pretreatment can be carried at any temperature, but it is preferably carried at the same temperature as the bleaching

5 stage, but however below 100°C.

In yet another embodiment of the process of the present invention the treatment comprises de-inking recycled fibre material in the aqueous medium containing the chelating agent, the polymer and the alkaline earth metal compound.

In the de-inking process the polymer composition according to the invention can

10 be used in repulping of wastepaper or in a disperger or in a kneader which possibly is followed by a soaking tower whereto hydrogen peroxide can be fed. In the de-inking process the polymer composition of the present invention can also be used in a separate bleaching stage or any process stage where hydrogen peroxide is present.

15 The pH in the alkaline bleaching, including the de-inking in the presence of hydrogen peroxide, is from 7 to 13, preferably from 7 to 12, and more preferably from 7 to 11.

The present invention is illustrated by following examples, which will not limit the scope of the invention.

20 In this specification the percentages are % by weight unless otherwise specified. In the tables below the amounts of chemicals given as kg refer to kg per ton dry pulp.

Example 1

Polymerization of AHPS and acrylic acid

25 Preparation of poly(acrylic acid-co-3-allyloxy-2-hydroxypropanesulfonic acid, sodium salt) aqueous solution; a 65:35 (mol) polymer.

A four-necked glass reactor of 0.25 liters, equipped with a heating/cooling jacket, an overhead stirrer, a thermometer, a reflux condenser, a gas inlet and 2 reagent pumps, was charged with 3-allyloxy-2-hydroxypropanesulfonic acid, sodium salt

30 40% aqueous solution (95.5g). The solution was degassed with nitrogen and temperature raised to 85°C. While the solution was stirred, there were pumped at constant rate acrylic acid 50% aqueous solution (46.8g) within 3 hours, and

sodium persulfate 1.3% aqueous solution (47.6g) within 3 hours and 30 minutes. The addition of the reagent solutions was started simultaneously. After addition of the sodium persulfate solution the reaction mixture was stirred for additional 1 hour and 30 minutes, while maintaining the temperature at 85°C. The reactor was 5 cooled, and slightly yellow and viscous aqueous copolymer solution was obtained.

A sample of the solution was treated with excess of concentrated hydrochloric acid solution to convert the corresponding sodium salts to free acids. Residual 3-allyloxy-2-hydroxypropanesulfonic acid content of the thus obtained solution was determined by gas chromatography, and was approximated to be 2.0 % by weight. 10 This refers to 90% conversion of the 3-allyloxy-2-hydroxypropanesulfonic acid, sodium salt monomer.

A sample of the first copolymer solution was neutralized with sodium hydroxide to pH about 10. The molecular weight of the thus obtained copolymer was determined by gel permeation chromatography against poly(acrylic acid, sodium 15 salt) standards. Number and weight average molecular weights were approximated to be 9,000 g/mol and 48,000 g/mol, respectively.

In order to make a preliminary test about the suitability of the stabilizers for alkaline peroxide solutions, stability tests were carried out, i.e. following the decomposition of hydrogen peroxide as a function of time. Since the results very 20 nicely followed the first order kinetics, the results are given as half life time figures. If a very low half life time is obtained, e.g. under some tens of minutes, the product is not suitable for alkaline peroxide bleaching. If the half life time is more than 100 minutes, the product may be suitable in alkaline peroxide bleaching without sodium silicate, but the result does not guarantee a good bleaching performance. 25 Since the transition metal ions, especially in wood abundantly present iron and manganese, will decompose alkaline hydrogen peroxide, the tests were carried out in the presence of these ions.

Following Examples 2 to 7 relate to stability tests of alkaline peroxide solutions and Examples 8 and 9 relate to laboratory peroxide bleaching tests.

30 **Example 2**

A solution containing Fe and Mn (as sulphates) and a stabilizer composition comprising one or more of following components: polymer (PAHPS-AA prepared in Example 1), Mg sulphate, and DTPA was prepared and pH adjusted to 10. The total amount of stabilizer in each test was 100 mg/l (calculated as active

substance). The temperature was raised to 50°C. The solution was stirred and hydrogen peroxide added in a concentration of 3 g/l. The pH was readjusted to 10, and the hydrogen peroxide concentration measured as a function of time (determined by standard iodometric method). The half life time of the hydrogen 5 peroxide was calculated according to 1st order reaction rate. Following stabilizer compositions were tested:

		Amount, mg/l (calculated as active substance)	
	DTPA	100	
	PAHPS-AA	100	
10	PAHPS-AA + DTPA	50 + 50	
	MgSO ₄	100	
	DTPA + MgSO ₄	80 + 20	
	PAHPS-AA + DTPA + MgSO ₄	40 + 40 + 20	

The results are shown in the table below.

	Molar shares					t _{1/2} , min (1 st order reaction rate)								
	Fe, ppm		Mn, ppm		Fe, mol-% Mn, mol-%	[Fe+Mn], μ mol/l	No stabilizer		DTPA	AHPS	PAHPS-AA + Mg DTPA	DTPA + PAHPS-AA + Mg		
	1.	4.0	0.0	75	100	0	72.2	892	45	61	8	880	260	1055
15	2.	3.0	1.0	25	75	25	72.2	16	57	8	224	35	254	1124
	3.	2.5	1.5	62	38	38	72.2	9	69	9	227	19	285	861
	4.	2.0	2.0	50	50	50	72.2	5	84	9	221	17	348	1043
	5.	1.5	2.5	37	63	63	72.2	2	94	9	225	11	517	1267
	6.	1.0	3.0	24	76	76	72.2	2	194	9	226	10	698	934
	7.	0.0	4.0	0	100	100	72.2	48	5317	8	228	10	51	620

The results clearly show the synergistic effect of the combination of these three chemicals, i.e. PAHPS-AA, DTPA and Mg. Since iron and manganese are the most abundant transition metals, and usually they both are present in mechanical pulps, it is very important to have good stabilizing performance in the presence of 20 these both metals.

Example 3

In this example some additional stabilizer compositions were tested. The tests were carried out in the same way as in Example 2. Following stabilizer compositions were tested:

		Amount, mg/l (calculated as active substance)
	ISA	100
	AES	100
5	DTPMPA	100
	ISA + PAHPS-AA + MgSO ₄	20 + 60 + 20
	AES + MgSO ₄	80 + 20
	PAHPS-AA + DTPA + DTPMPA + MgSO ₄	50 + 15 + 15 + 20
	PAHPS-AA + AES + MgSO ₄	40 + 40 + 20

10

The results are shown in the table below.

Fe, ppm	Mn, ppm	Molar shares			[Fe+Mn], $\mu\text{mol/l}$	t _{1/2} , min (1 st order reaction rate)			
		Fe, mol-%	Mn, mol-%	No stabilizer		ISA	AES	DTPMPA	
1.	4.0	0.0	100	0	72.2	892	376	14001	376
2.	3.0	1.0	75	25	72.2	16	21	222	81
3.	2.5	1.5	62	38	72.2	9	9	274	64
4.	2.0	2.0	50	50	72.2	5	9	322	60
5.	1.5	2.5	37	63	72.2	2	9	386	71
6.	1.0	3.0	24	76	72.2	2	9	549	164
7.	0.0	4.0	0	100	72.2	48	592	242	1962

	ISA+ PAHPS-AA+ Mg	AES+ Mg	PAHPS-AA+ DTPA+ DTPMPA+ Mg	PAHPS-AA+ AES+ Mg
1.	1089	587	2992	8455
2.	1027	1255	2594	1145
3.	745	513	2099	827
4.	671	199	1487	614
5.	601	31	876	338
6.	482	28	549	333
7.	36	29	260	264

15 The results show that very good results were obtained by the stabilizer compositions of the present invention

Example 4

The effect of the composition of the stabilizer is shown in the table below. The tests were carried out in the same way as in Example 2.

Fe, ppm	Mn, ppm	PAHPS-AA, %	DTPA, %	Mg, %	Stabilizer, mg/l	t 1/2, min
1	3	80	0	20	100	682
1	3	60	20	20	100	955
1	3	50	30	20	100	992
1	3	40	40	20	100	1443
1	3	30	50	20	100	1979
1	3	20	60	20	100	2294
1	3	10	70	20	100	734
1	3	0	80	20	100	607

5

As can be seen from the table, the combination of the polymer, the complexing agent and the alkaline earth metal compound has better performance than the combination of the polymer and the alkaline earth metal compound and the combination of the complexing agent and the alkaline earth metal compound.

10 Example 5

In this example, the effect of the concentration of alkaline earth metal is demonstrated. The tests were carried out in the same way as in Example 2.

Fe, ppm	Mn, ppm	PAHPS-AA, %	DTPA, %	Mg, %	Stabilizer, mg/l	t 1/2, min
1	3	50	50	0	100	226
1	3	45	45	10	100	736
1	3	40	40	20	100	1443
1	3	35	35	30	100	1001
1	3	25	25	50	100	211
1	3	15	15	70	100	29
2	2	45	45	10	100	425
2	2	40	40	20	100	2376
2	2	35	35	30	100	1164
2	2	30	30	40	100	738

15 As can be seen from this example, there exists a certain optimal composition that gives the best stability.

Example 6

In this example, the effect of the total concentration of the stabilizers is demonstrated. The tests were carried out in the same way as in Example 2.

Fe, ppm	Mn, ppm	PAHPS-AA, mg/l	DTPA, mg/l	Mg, mg/l	Stabilizer, mg/l	t 1/2, min
1	3	0	0	0	0	10
1	3	20	20	10	50	922
1	3	30	30	15	75	1514
1	3	40	40	20	100	2294
1	3	60	60	30	150	2993

5

Example 7

This example shows how the optimal PAHPS-AA: DTPA ratio changes when iron and manganese concentration changes. The tests were carried out in the same way as in Example 2.

10

Fe, ppm	Mn, ppm	PAHPS-AA, %	DTPA, %	Mg, %	Stabilizer, mg/l	t 1/2, min
2	2	20	60	20	100	1307
2	2	40	40	20	100	2376
1	3	20	60	20	100	2294
1	3	40	40	20	100	1443

Example 8

An industrial TMP (spruce, *picea abies*) pulp was bleached in laboratory using different stabilizers. The pulp contained 6 ppm Fe, 8 ppm Mn, 730 ppm Ca, and <

15 2 ppm Cu. The PAHPS-AA used in this test was prepared in Example 1. DTPA used in this test was of commercial grade containing the normal side products of the process. The reaction temperature was 70°C, reaction time 120 minutes, consistency 12%. Chemical charges were: NaOH 35 kg/ton pulp, H₂O₂ 45 kg/ton pulp, stabilizer dosages are shown in table below (calculated as active substance).
 20 Initial pH in the bleaching was 10.4-10.2.

PAHPS-AA, kg	1.3	0.8	0.6	0.4	0	0
Na ₅ DTPA, kg	1.3	0.8	0.6	0.4	0	0
Mg, kg	0.63	0.42	0.28	0.19	0	0
Stabilizer, as 100%, kg	3.13	2.10	1.41	0.94	0	0
Waterglass, kg/ton pulp	0	0	0	0	0	25
Residual H ₂ O ₂	17.5	18.7	15.6	16	2	17.3
Brightness	77.8	78.6	77.7	77.7	75	77.6
According to the invention?	Yes	Yes	Yes	Yes	No	No

The results show, that silicate can be efficiently replaced by the stabilizer according to this invention.

Example 9

5 In this example, the effect of pH in bleaching is demonstrated. The pulp used in this test is the same as in example 8. The detailed reaction conditions and chemical dosages are presented in the table below.

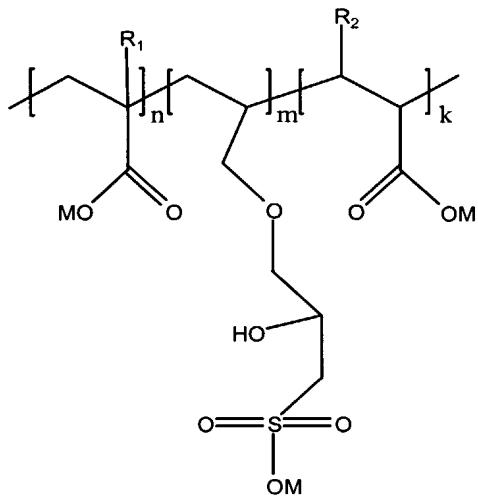
no	107	108	102	103	104	105	106	113	114	115	116
test	P	P	P	P	P	P	P	P	P	P	P
T,C	70	70	70	70	70	70	70	70	70	70	70
t,min	120	120	120	120	120	120	120	120	120	120	120
Cs,%	12	12	12	12	12	12	12	12	12	12	12
Initial pH	10.3	10.4	10.5	10.3	10.1	10	10.1	10.4	10.3	10.1	10
Final pH	9.7	9.7	9.4	9	8.5	8.5	8.5	9.8	9.7	9.5	9
H ₂ O ₂ , kg	45	45	45	45	45	45	45	45	45	45	45
NaOH, kg	38	38	35	30	25	25	25	38	35	30	25
Waterglass, kg	0	0	0	0	0	0	0	25	25	25	25
DTPA, kg	2.5	1.25	2.5	2.5	1.75	1	0	0	0	0	0
PAHPS-AA, kg	2.5	1.25	2.5	2.5	1.75	1	0	0	0	0	0
MgSO ₄ , kg/t	3.1	1.6	3.1	3.1	3.1	2.2	1.3	0	0	0	0
Residual H ₂ O ₂ ,kg	17.4	16.8	21.8	27.2	31.5	30.2	27.8	16.2	17.3	28	32
Residual NaOH,kg	3.4	4	2.4	1.2	0.6	0.7	0.7	8.6	7.1	4.8	2.3
Brightness,% ISO	77	77.3	77.8	77.2	76.7	76.7	76.3	77.5	77.6	77.4	77.1
According to the invention?	Yes	No	No	No	No						

10 pH is a very significant factor in bleaching. Higher alkalinity leads to lower stability of peroxide. On the other hand higher alkalinity improves bleaching performance by increasing perhydroxyl anion concentration. This example shows that the stabilizer according to this invention gives bleaching result equal to sodium silicate even with high alkali charge.

Claims

1. A stabilizing composition comprising following components

(A) a polymer having following formula



5 wherein

R₁ is a hydrogen atom or an alkyl group containing 1 to 12 carbon atoms,

R₂ is -COOM or -CH₂COOM,

M is a hydrogen atom, an alkali metal ion, an alkaline earth metal ion, an ammonium ion or a mixture thereof,

10 n, m and k are molar ratios of corresponding monomers, wherein n is 0 to 0.95, m is 0.05 to 0.9, and k is 0 to 0.8, and (n+m+k) equals 1, and

the weight average molecular weight is between 500 and 20,000,000 g/mol,

(B) a chelating agent, and

(C) an alkaline earth metal compound.

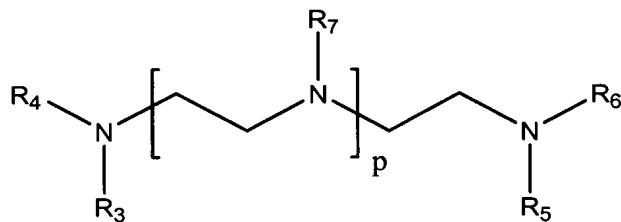
15 2. The composition according to claim 1 wherein in formula I n is 0.4 to 0.9, m is 0.1 to 0.5, and k is 0 to 0.5.

3. The composition according to claim 1 or 2 wherein the weight average molecular weight of the copolymer is between 1,000 and 1,000,000 g/mol and preferably between 2,000 g/mol and 500,000 g/mol.

4. The composition according to any of claims 1 to 3 wherein the three components (A), (B) and (C) are present in following weight ratios 10 to 60 : 20 to 70 : 10 to 50, preferably 15 to 55 : 25 to 65 : 15 : 45, more preferably 20 to 50 : 30 to 60 : 20 to 40 calculated as active substance.

5 5. The composition according to any of claims 1 to 4 wherein the polymer is a copolymer of 3-allyloxy-2-hydroxypropanesulfonic acid and at least one of the monomers acrylic acid, methacrylic acid, maleic acid and itaconic acid or a salt thereof.

6. The composition according to any of claims 1 to 5 wherein the chelating 10 agent is a compound having following general formula

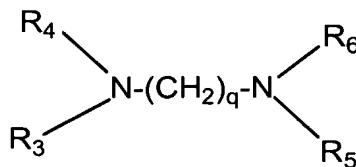


wherein

p is 0 or an integer of 1 to 10,

15 R_3 , R_4 , R_5 , R_6 and R_7 are independently a hydrogen atom or an alkyl chain having 1 to 6 carbon atoms and containing one or more active chelating ligands, such as carboxylic, phosphonic or hydroxyl group(s) or a salt thereof.

7. The composition according to any of claims 1 to 5 wherein the chelating agent is a compound having following general formula

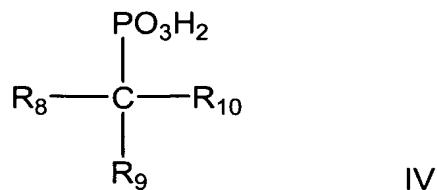


wherein

q is an integer of 3 to 10,

R_3 , R_4 , R_5 and R_6 are independently a hydrogen atom or an alkyl chain having 1 to 6 carbon atoms and containing one or more active chelating ligands, such as carboxylic, phosphonic or hydroxyl group(s) or a salt thereof.

8. The composition according to any of claims 1 to 5 wherein the chelating
5 agent is a compound having following general formula



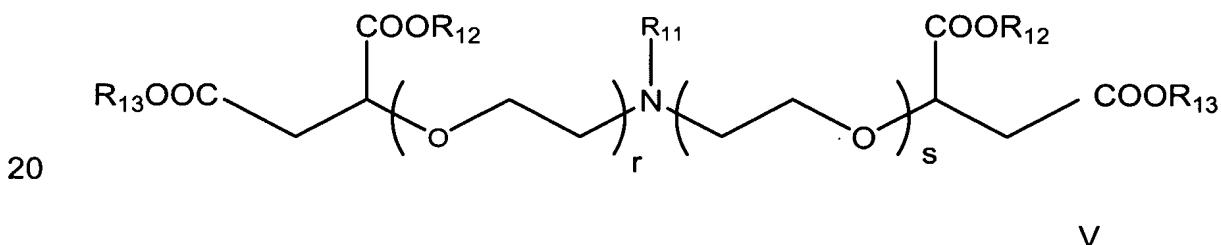
wherein

10 R₈ is a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms or an alkyl chain having 1 to 6 carbon atoms and containing a carboxylic, phosphonic or hydroxyl group,

R₉ is a hydrogen atom, hydroxyl group, phosphonic group, carboxylic group or alkyl chain having 1 to 6 carbon atoms and containing one or two carboxylic groups, and

15 R₁₀ is a hydrogen atom, hydroxyl group, carboxylic group, alkyl group containing 1 to 6 carbon atoms or alkyl chain having 1 to 6 carbon atoms and containing a carboxylic group, or a salt thereof.

9. The composition according to any of claims 1 to 5 wherein the chelating agent is a compound having following general formula



wherein R_{11} is
a hydrogen atom

an alkyl chain containing 1-30 carbon atoms,
an alkyl chain containing 1-30 carbon atoms and 1-10 carboxylic acid groups attached to said chain, or alkali or alkaline earth metal salt thereof,
an alkyl chain containing 1-30 carbon atoms and 1-10 carboxylic acid esters
5 attached to said chain,
a (poly)ethoxylated hydrocarbon chain containing 1-20 ethoxyl groups, or
a carboxylic acid amide containing 1-30 carbon atoms, where N-R₁₁ bond is an amide bond,
R₁₂ and R₁₃ are: hydrogen, an alkali metal ion or an alkaline earth metal ion or an
10 alkyl group containing 1-30 carbon atoms,
r is 0 or 1, and
s is 0 or 1.

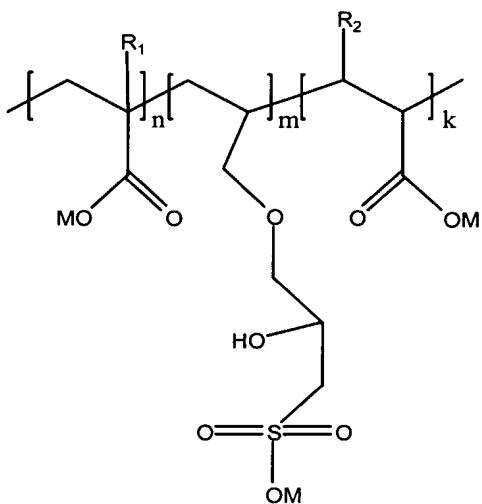
10. The composition according to any of claims 1 to 9 wherein the alkaline earth metal compound is a water-soluble magnesium or calcium salt, such as
15 magnesium or calcium chloride, sulphate or acetate or a mixture thereof, preferably magnesium sulphate.

11. Use of a composition according to any of claims 1 to 10 as a stabilizer in bleaching of a fibre material in an aqueous medium.

12. Use of a composition according to any of claims 1 to 10 as a stabilizer in
20 deinking of a recycled fibre material.

13. A process for the treatment of a fibre material comprising the step of contacting the fibre material in an aqueous medium with following components

(A) a polymer having following general formula



I

wherein

R_1 is a hydrogen atom or an alkyl group containing 1 to 12 carbon atoms,

R_2 is $-COOM$ or $-CH_2COOM$,

5 M is a hydrogen atom, an alkali metal ion, an alkaline earth metal ion, an ammonium ion or a mixture thereof,

n, m and k are molar ratios of corresponding monomers, wherein n is 0 to 0.95, m is 0.05 to 0.9, and k is 0 to 0.8, and $(n+m+k)$ equals 1, and

the weight average molecular weight is between 500 and 20,000,000 g/mol,

10 (B) a chelating agent, and

(C) an alkaline earth metal compound.

14. The process according to claim 13 wherein the three components (A), (B) and (C) are introduced as a mixture or the three components (A), (B) and (C) are introduced separately.

15 15. The process according to claim 13 or 14 wherein the fibre material is a cellulosic fibre material comprising a chemical, mechanical or chemi-mechanical pulp or a recycled fibre material.

16. The process according to any of claims 13 to 15 wherein the treatment comprises bleaching the fibre material with an alkaline peroxide solution in the presence of the three components (A), (B) and (C).

17. The process according to claim 16 wherein the bleaching is preceded by a treatment with a chelating agent.
18. The process according to any of claims 13 to 15 wherein the treatment comprises pretreating the fibre material in the aqueous medium comprising the three components (A), (B) and (C).
19. The process according to claim 18 wherein the pH of the aqueous medium in the pretreatment is between 3 and 7, preferably between 4 and 6.5, and more preferably between 4.5 and 6.
20. The process according to claim 18 or 19 wherein the pretreatment is followed by a bleaching with a peroxygen compound optionally in the presence of the three components (A), (B) and (C).
21. The process according to claim 20 wherein the peroxygen compound is hydrogen peroxide, peracetic acid or Caro's acid.
22. The process according to claim 13 or 14 wherein the fibre material comprises a recycled fibre material, and wherein the treatment comprises de-inking the recycled fiber material in the aqueous medium comprising the three components (A), (B) and (C).
23. The process according to any of claims 13 to 22 wherein in formula I n is 0.4 to 0.9, m is 0.1 to 0.5, and k is 0 to 0.5.
24. The process according to any of claims 13 to 23 wherein the weight average molecular weight of the copolymer is between 1,000 and 1,000,000 g/mol and preferably between 2,000 g/mol and 500,000 g/mol.
25. The process according to any of claims 13 to 24 wherein the total amount of the three components in the treatment is 0.05 to 10 kg per ton of dry fibre material, preferably 0.1 to 5 kg per ton of dry fibre material, and more preferably 0.2 to 4 kg per ton of dry fibre material.
26. The process according to any of claims 13 to 25 wherein the three components (A), (B) and (C) are present in following weight ratios 10 to 60 : 20 to 70 : 10 to 50, preferably 15 to 55 : 25 to 65 : 15 : 45, more preferably 20 to 50 : 30 to 60 : 20 to 40 calculated as active substance.

27. The process according to any of claims 13 to 26 wherein the polymer is a copolymer of 3-allyloxy-2-hydroxypropanesulfonic acid and at least one of the monomers acrylic acid, methacrylic acid, maleic acid and itaconic acid or a salt thereof.

5 28. The process according to any of claims 13 to 27 wherein the chelating agent and the alkaline earth metal compound are as defined in any of claims 6 to 10.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FI2005/000211

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21C9/16 D21C9/10 D21C5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 014, no. 030 (C-678), 19 January 1990 (1990-01-19) & JP 01 266295 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 24 October 1989 (1989-10-24) cited in the application abstract -----	1-28
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 18, 5 June 2001 (2001-06-05) & JP 01 148890 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 12 June 1989 (1989-06-12) cited in the application abstract ----- -/-	1-28 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

12 September 2005

23/09/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Naeslund, P

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI2005/000211

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 2 441 841 A1 (UNIVERSITY OF NEW BRUNSWICK) 23 March 2004 (2004-03-23) examples 1,2 claim 1 -----	1-28
Y	DATABASE WPI Section Ch, Week 198601 Derwent Publications Ltd., London, GB; Class D25, AN 1986-004442 XP002344420 & JP 60 231876 A (AIR LIQUIDE L) 18 November 1985 (1985-11-18) abstract -----	1-28
Y	WO 90/11403 A (HYMAC LTD) 4 October 1990 (1990-10-04) page 3, line 34 – page 5, line 23 -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/FI2005/000211

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
JP 01266295	A 24-10-1989	JP 1720923 C JP 4003478 B		24-12-1992 23-01-1992
JP 01148890	A 12-06-1989	JP 1723034 C JP 4009232 B		24-12-1992 19-02-1992
CA 2441841	A1 23-03-2004	US 2003070777 A1		17-04-2003
JP 60231876	A 18-11-1985	NONE		
WO 9011403	A 04-10-1990	CA 1340348 C AT 106961 T WO 9011403 A1 DE 69009750 D1 EP 0464110 A1		26-01-1999 15-06-1994 04-10-1990 14-07-1994 08-01-1992